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An efficient molybdenum disulfide/cobalt diselenide hybrid catalyst for electrochemical hydrogen generation

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The electroreduction of water for sustainable hydrogen production is a critical component of several developing clean-energy technologies, such as water splitting and fuel cells. However, finding a cheap and efficient alternative catalyst to replace currently used platinum-based catalysts is still a prerequisite for the commercialization of these technologies. Here we report a robust and highly active catalyst for hydrogen evolution reaction that is constructed by *in situ* growth of molybdenum disulfide on the surface of cobalt diselenide. In acidic media, the molybdenum disulfide/cobalt diselenide catalyst exhibits fast hydrogen evolution kinetics with onset potential of -11 mV and Tafel slope of 36 mV per decade, which is the best among the non-noble metal hydrogen evolution catalysts and even approaches to the commercial platinum/carbon catalyst. The high hydrogen evolution activity of molybdenum disulfide/cobalt diselenide hybrid is likely due to the electrocatalytic synergistic effects between hydrogen evolution-active molybdenum disulfide and cobalt diselenide materials and the much increased catalytic sites.

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Owing to their diffuse nature, electricity from renewable but intermittent energy (for example, solar and wind) must be stored durably for off-grid applications. Electrochemical water splitting to produce hydrogen (H_2) offers a promising and sustainable solution for this purpose by converting such electricity energy into stable chemical bonds^{1,2}. Appropriate electrocatalysts, such as platinum (Pt) and its alloys, play a vital role in the H_2 evolution reaction (HER) because they can catalyse the conversion from a pair of protons and electrons to H_2 at high reaction rates and low overpotentials (η)^{1–3}. However, the prohibitive cost and scarcity of Pt pose tremendous limitations to widespread use. Therefore, finding robust and efficient alternative catalysts that are geologically abundant is crucial to the future of ‘hydrogen economy’.

Molybdenum disulfide (MoS_2), a widely used industrial catalyst for hydrosulfurization⁴, has recently demonstrated promise as effective HER catalyst based on both computational and experimental studies^{5,6}. The HER activity was discovered to arise from the exposed (10–10) planes on edges of MoS_2 , whereas the (0001) basal planes are catalytically inactive^{5–7}. This understanding has led to great efforts to develop highly nanostructured MoS_2 -based HER catalysts to maximize the number of edge sites, including crystalline^{8–12} and amorphous materials^{13–15}, MoS_2 -based hybrid materials^{16–19} and molecular mimics⁷. Despite significant success, the design and fabrication of MoS_2 -based HER electrocatalysts with satisfactory activity and stability remain a big challenge.

In recent years, we have been making efforts to explore efficient electrocatalysts by using Earth-abundant 3d metal (Co, Ni and so on) chalcogenides^{20–27}. New NiSe nanofibres²⁴ and lamellar mesostructured $CoSe_2$ /DETA (DETA, diethylenetriamine) nanobelts²⁵ were found to show decent HER activity in acidic electrolyte. Kong *et al.*²⁸ also observed good HER activities from various polycrystalline transition metal dichalcogenide (ME_2 , $M = Fe, Co, Ni$; $E = S, Se$) films, especially from the $CoSe_2$. Recently, we found that the HER activity of $CoSe_2$ nanobelts can be improved greatly after anchoring Ni/NiO nanoparticles onto their surfaces²⁵. The synergetic chemical coupling effects between $CoSe_2$ and grafted Ni/NiO were believed to contribute to the enhancement. Similar promoted performances have also been observed on MoS_2 /graphene^{16,17}, MoO_3 / MoS_2 (ref. 18) and MoS_2 /Au (ref. 19) composite catalysts for H_2 production. These works point to the possibility to access new and efficient HER catalysts by combining the promising $CoSe_2$ and MoS_2 .

We report here that a HER electrocatalyst based on quasi-amorphous MoS_2 -coated $CoSe_2$ (denoted as $MoS_2/CoSe_2$) hybrid is highly active and stable in acidic electrolyte. Notably, without any noble metals, the $MoS_2/CoSe_2$ hybrid catalyst shows an onset potential close to commercial Pt catalyst (Johnson-Matthey, 20 wt% Pt/XC-72) and a small Tafel slope of ~ 36 mV per decade as well as no current loss after long-term chronoamperometry measurement, performing the best among the noble-metal-free HER electrocatalysts. These results suggest a strategy for designing non-noble metal catalysts with enhanced HER performance that is comparable to the state-of-the-art Pt-based catalysts.

Results

$MoS_2/CoSe_2$ hybrid catalyst. The $MoS_2/CoSe_2$ hybrid was prepared directly in a closed *N,N*-dimethylformamide (DMF)/hydrazine solvothermal system, where $(NH_4)_2MoS_4$ was used as a precursor for growing MoS_2 around the freshly made $CoSe_2$ /DETA nanobelt substrates (Fig. 1a; Supplementary Fig. 1; see Methods for details of the synthesis). The MoS_2 -coated $CoSe_2$

hybrid was shown by means of scanning electron microscopy and transmission electron microscopy (TEM; Fig. 2a–c), which revealed the compact graphene-like MoS_2 nanosheets grown on the surface of $CoSe_2$ with a partially free-standing branch-like feature (Supplementary Fig. 2). Substantial amino groups on the $CoSe_2$ /DETA surface (Supplementary Fig. 3) serve as nucleation sites for coupling Mo precursor and subsequently reduced to MoS_2 on $CoSe_2$ (refs 21,23). A control experiment performed under identical synthesis conditions, but without $CoSe_2$ nanobelts, produced three-dimensional (3D) aggregates of MoS_2 sheets (Fig. 1b; Supplementary Fig. 4), suggesting that $CoSe_2$ could be a useful support for mediating the growth of loaded materials and constructing novel functional hybrids.

Figure 2d presents high-resolution TEM (HRTEM) images of the $MoS_2/CoSe_2$ hybrid. Layered MoS_2 (often less than five layers) nanosheets, with an interlayer separation of 0.63 nm, were grown intimately on the $CoSe_2$ substrate. High-crystalline $CoSe_2$ substrate with *d* spacing of 0.27 nm can be seen frequently through the interspace of grafted MoS_2 (see Supplementary Fig. 5 for additional images). This non-fully covered structure may take advantage of merits from both MoS_2 and $CoSe_2$ for catalysing H_2 evolution. Selected area electron diffraction (SAED) pattern (inset in Fig. 2c; Supplementary Fig. 6) revealed clear diffraction spots (marked by yellow arrows) from single-crystalline $CoSe_2$ support (JCPDS 9-0234) and also faint diffraction rings from grafted MoS_2 (JCPDS 77-1716). These barely recognizable diffraction rings indicate the quasi-amorphous structure of MoS_2 , consistent with the X-ray diffraction (XRD) data of $MoS_2/CoSe_2$ with broadening diffraction peaks (Fig. 2e). Inasmuch as amorphous MoS_2 has recently been demonstrated to be effective HER catalysts^{13–15} for its abundant defects and resultant more active edge sites²⁹, we thus infer that the quasi-amorphous MoS_2 modification may benefit the hybrid material to catalytically evolve H_2 . Energy-dispersive X-ray spectrum (EDX; Fig. 2f) analysis further confirmed the formation of $MoS_2/CoSe_2$ hybrid with Co, Se, Mo and S as the principal elemental components (Cu and C peaks emanate from the carbon-coated TEM grid), agreeing with the X-ray photoelectron spectroscopy (XPS) results (Supplementary Fig. 7). Scanning TEM (STEM) and EDX elemental mappings revealed uniform spatial distribution of Co, Se, Mo and S over the marked detection range of the constructed hybrid material (Fig. 2g).

Catalytic hydrogen evolution. To assess the HER electrocatalytic activity, thin film of various catalysts was prepared on glassy carbon (GC) electrodes for cyclic voltammetry in H_2 -saturated 0.5 M H_2SO_4 electrolyte (see Methods for experimental details). Potentials were measured vs saturated calomel electrode (SCE) and are reported vs reversible hydrogen electrode (RHE). The electrode was kept rotating (1,600 r.p.m.) during the measurements to remove *in situ*-emerged H_2 bubbles. Figure 3a shows that GC electrode guarantees a minimal background activity for H_2 evolution. A reductive sweep of $MoS_2/CoSe_2$ hybrid showed a low η of 11 mV for the HER, beyond which a sharp increase in cathodic current was observed, corresponding to catalytic H_2 evolution (Fig. 3a; Supplementary Fig. 9). By contrast, pure $CoSe_2$ nanobelts exhibited inferior HER activity with a larger onset potential of ~ 50 mV and lower catalytic current, while pure MoS_2 nanosheet aggregates only affected little HER activity. The HER kinetics of the above catalysts was probed by corresponding Tafel plots ($\log j \sim \eta$) (Fig. 3b). Tafel slope of ~ 36 mV per decade was measured for $MoS_2/CoSe_2$ hybrid, which is close to the value of 30 mV per decade for Pt/C catalyst and lower than that of 48 mV per decade for $CoSe_2$ and 101 mV per decade for 3D MoS_2 aggregates (Table 1). This Tafel slope is also comparable to or

Figure 1 | Schematic illustration of the preparation of MoS₂/CoSe₂ hybrid. (a) Solvothermal synthesis with CoSe₂/DETA nanobelts as substrates for preparation of MoS₂/CoSe₂ hybrid. **(b)** Solvothermal synthesis without CoSe₂/DETA nanobelts leads to free MoS₂ nanosheet aggregates.

Figure 2 | Characterization of the MoS₂/CoSe₂ hybrid. (a) Scanning electron microscopy image of MoS₂/CoSe₂ hybrid. Scale bar, 800 nm. **(b,c)** TEM images with different magnifications of MoS₂/CoSe₂ hybrid. Scale bars, 200 and 50 nm, respectively. The inset in **c** shows corresponding SAED pattern. **(d)** HRTEM images of MoS₂/CoSe₂ hybrid showing distinguishable microstructures of MoS₂ and CoSe₂. Scale bars, 5 nm. **(e,f)** XRD patterns and EDX spectrum of the MoS₂/CoSe₂ hybrid, respectively. **(g)** STEM-EDX elemental mapping of MoS₂/CoSe₂ hybrid showing clearly the homogeneous distribution of Co (red), Se (green), Mo (yellow) and S (blue). Scale bars, 200 nm.

lower than that of all the reported noble-metal-free HER catalysts in the literature (Supplementary Table 1), demonstrating the superior HER kinetics of MoS₂/CoSe₂ hybrid. At high current densities (for example, 10 mA cm⁻² with η of 68 mV), MoS₂/CoSe₂ hybrid also represents a more efficient catalyst relative to

other noble-metal-free HER catalysts (Supplementary Table 1). The HER inherent activity of these catalysts was evaluated by the exchange current density (j_0). The j_0 of 7.3×10^{-2} mA cm⁻² for MoS₂/CoSe₂ hybrid outperforms the values of 8.4×10^{-3} mA cm⁻² for pure CoSe₂ and 9.1×10^{-4} mA cm⁻² for pure

Figure 3 | Electrocatalytic hydrogen evolution of different catalysts. (a) Polarization curves for HER on bare GC electrode and modified GC electrodes comprising MoS₂/CoSe₂ hybrid, pure MoS₂, pure CoSe₂ and a high-quality commercial Pt/C catalyst. Catalyst loading is about 0.28 mg cm⁻² for all samples. Sweep rate: 2 mV s⁻¹. (b) Tafel plot for the various catalysts derived from a. (c) Chronoamperometric responses ($j \sim t$) recorded on MoS₂/CoSe₂ hybrid and pure MoS₂ at a constant applied potential of -0.7 V vs SCE. The catalysts were deposited on CFP with the same loading of 1 mg cm⁻². Inset digital photos show the H₂ bubbles formed on MoS₂-modified CFP (up) and MoS₂/CoSe₂-modified CFP (down) at the time point of 20 h. All the measurements were performed in H₂-saturated 0.5 M H₂SO₄ electrolyte. dec, decade.

Table 1 | Comparison of catalytic parameters of different HER catalysts.

Catalyst	Onset potential (mV vs RHE)	Tafel slope (mV per decade)	Exchange current density (j_0 , mA cm ⁻²)*
MoS ₂	-237	101	9.1×10^{-4}
CoSe ₂	-50	48	8.4×10^{-3}
MoS ₂ /CoSe ₂	-11	36	7.3×10^{-2}
Pt/C†	0	30	7.1×10^{-1}

HER, H₂ evolution reaction; RHE, reversible hydrogen electrode.
 * j_0 were calculated from Tafel curves using extrapolation method.
 †Johnson-Matthey, 20 wt% Pt/XC-72.

MoS₂ (Table 1) and also the j_0 value for most of the reported noble-metal-free HER catalysts (Supplementary Table 1). The high electrode kinetic metrics (including onset potential of -11 mV and the Tafel slope of 36 mV per decade) and large j_0 (only ~1 order of magnitude lower than the value of 7.1×10^{-1} mA cm⁻² for Pt) highlight the exceptional H₂ evolving efficiency of the new MoS₂/CoSe₂ hybrid catalyst.

Material stability. The long-term stability of MoS₂/CoSe₂ hybrid catalyst was assayed by means of chronoamperometry measurement ($j \sim t$) with a high catalyst loading of 1 mg cm⁻² on carbon fibre paper (CFP). This quasi-electrolysis process was performed at a constant potential of -0.7 V vs SCE in 0.5 M H₂SO₄ for 24 h. As shown in Fig. 3c, the current density of MoS₂/CoSe₂-modified CFP electrode decreased gradually at the initial 3 h, which then increased quickly over 24 h of continuous operation. We hypothesize that the more efficient HER-active sites in our hybrid materials are the interfaces between MoS₂ and CoSe₂, where Co from the support materials could promote the HER kinetics by

Figure 4 | S 2p XPS spectrum analysis. S 2p XPS spectra for pure MoS₂, MoS₂/CoSe₂ hybrid and MoS₂/CoSe₂ hybrid after stability test. The top right corner demonstrates the structure model of MoS₂/CoSe₂ hybrid.

lowering the Gibbs free energy of adsorbed hydrogen (ΔG_H)^{8,29,30}. The severe reducing condition at the initial 3 h caused degradation of external MoS₂ and allowed more electrolyte to access the MoS₂-CoSe₂ interfaces (Supplementary Fig. 11; Supplementary Note 1; Supplementary Table 2), yielding the increased HER current density. Remarkably, after 24 h of operation, XPS studies revealed no obvious chemical state change of HER-active S (Fig. 4) and the homogeneous elemental distribution was maintained (Supplementary Fig. 12; Supplementary Note 1), suggesting the robustness of the hybrid

Figure 5 | HER mechanism. Reaction pathway of HER on MoS₂/CoSe₂ hybrid according to the Volmer–Tafel route. The calculated distance of two hydrogen atoms and energies are displayed in Å and eV. Blue, orange, azure, yellow and pink indicate Co, Se, Mo, S and H atoms, respectively.

catalyst. By comparison, under the exact same condition, the pure MoS₂ catalyst exhibited a slow but continuous decrease in HER activity. Furthermore, digital photo (inset in Fig. 3c) taken from MoS₂/CoSe₂-modified CFP electrode showed vigorous effervescence at 20 h (also Supplementary Movie 1), comparing favourably with the H₂ bubbles formed on free MoS₂-modified electrode. The exceptional long-term durability of our MoS₂/CoSe₂ hybrid catalyst suggests the promise for implementing this new catalyst into realistic hydrogen evolution electrode.

HER-enhanced mechanism. The experimentally observed high HER intrinsic activity ($j_0 = 7.3 \times 10^{-2} \text{ mA cm}^{-2}$) of MoS₂/CoSe₂ hybrid catalyst prompted us to probe the enhanced mechanism. Generally, the value of ΔG_H is considered as a reasonable descriptor of HER activity for a wide variety of catalysts^{3,30,31}. An optimum HER activity is suggested to be achieved at value of $\Delta G_H \approx 0$ (ref. 30). Lower ΔG_H will lead to very high surface coverage of H_{ads} , while higher ΔG_H will make the protons bonded too weakly on the catalyst surface, which both lead to the slow HER kinetics^{3,30,31}. Previous density functional theory (DFT) calculations⁵ showed that MoS₂ edge sites with unsaturated sulfur atoms can lower the ΔG_H approaching to 0 and thus are active for HER, which was later proved by Jaramillo *et al.*⁶ experimentally. Recently, Hu and co-workers^{13,14} found that amorphous MoS₂ films are particularly HER active and the increased coordinately and structurally unsaturated sulfur atoms led to the enhancement. Furthermore, first-row transition metal ions, especially Co, can promote the HER activity of MoS₂ by coupling with S-edges to lower their ΔG_H from 0.18 to 0.10 eV to afford a faster proton adsorption kinetics^{8,29,30}. As to MoS₂/CoSe₂ hybrid catalyst, the quasi-amorphous MoS₂ around the CoSe₂ may bring in more active edge sites. Meanwhile, the CoSe₂ chemically interacts with MoS₂ by forming S–Co bond (Fig. 4 and inset), similar to the XPS peak observed in Co-promoted MoS₃ film³², which can further improve the HER activity of MoS₂. By contrast, no such XPS peak was found in Fig. 4 for pure MoS₂ catalyst. XPS analyses of the S 2*p* region also exhibit a dramatically decreased electron-binding energy (by ~ 1.3 eV) after growing MoS₂ on the CoSe₂, suggesting the formation of more terminal S₂^{2−} and S^{2−} ions, which are HER active (Fig. 4)^{14,19}. Therefore, the CoSe₂ nanobelts, a material with decent HER activity by itself, can not only chemically couple with MoS₂ to promote the HER activity, but also serve as an effective support for mediating the growth of MoS₂ to form more terminal S₂^{2−} and S^{2−}. Meanwhile, anchored MoS₂ may also boost the HER-active sites of CoSe₂ and these electrocatalytic synergistic effects³³ together lead to the high HER performance of MoS₂/CoSe₂ hybrid catalyst.

For the HER in acidic media, two separate pathways (the Volmer–Tafel or the Volmer–Heyrovsky mechanism) have been proposed for reducing H^+ to H₂ (refs 30,34). Specifically, the two distinct mechanisms involve three principal steps, referring to the

Volmer (electrochemical hydrogen adsorption: $H_3O^+ + e^- \rightarrow H_{\text{ads}} + H_2O$), the Heyrovsky (electrochemical desorption: $H_{\text{ads}} + H_3O^+ + e^- \rightarrow H_2^{\uparrow} + H_2O$) and the Tafel (chemical desorption: $H_{\text{ads}} + H_{\text{ads}} \rightarrow H_2^{\uparrow}$) reactions^{30,34}. Tafel slope, an intrinsic property of electrocatalysts, could be used to probe the elementary steps involved in the H₂ evolution. For example, HER kinetic models suggest that Tafel slope of about 120, 40 or 30 mV per decade will be obtained if the Volmer, Heyrovsky or Tafel reaction is the rate-determining step, respectively³⁴. The Tafel slope down to ~ 36 mV per decade for MoS₂/CoSe₂ in 0.5 M H₂SO₄ is the lowest value measured till now for MoS₂-based HER catalysts (Supplementary Table 1), even approaching to that of ~ 30 mV per decade for Pt/C catalysts. This Tafel slope suggests a Tafel-step-determined Volmer–Tafel mechanism works in the MoS₂/CoSe₂ catalyst, where the synergistic CoSe₂ substrate with decent HER activity presumably contributes to this HER mechanism.

Considering that at least one decade of linearity in Tafel extrapolation at relatively large η is desirable to ensure an accurate Tafel analysis, the calculated Tafel slopes (Fig. 3b) and derived HER mechanism may be inconclusive. To prove the proposed HER mechanism, we performed a computational study on the new MoS₂/CoSe₂ catalyst to gain detailed insights into the adsorption, activation and reaction processes (Fig. 5; see Supplementary Methods for computational details). DFT calculations suggested that reactant (R) contains two H atoms adsorbed on different sites of the optimized MoS₂/CoSe₂ model with H–H distance of 2.134 Å. Two approached H atoms on the side S atoms of MoS₂ cluster then formed a transition state (TS) with H–H distance of 0.945 Å and imaginary vibration frequency of 828i cm^{−1}. After crossing the TS, product (P) with a weakly adsorbed H₂ molecule (0.745 Å) was formed. The calculated activation barrier of 1.13 eV (30.7 kcal mol^{−1}) for the Tafel-step reaction on MoS₂/CoSe₂ hybrid, which can be overcome at a slightly higher η , approaches that of Pt (111) electrode³⁵, agreeing well with our experimentally observed fast HER kinetics.

Discussion

In conclusion, we demonstrate that an effective and robust hydrogen evolution catalyst can be made by marrying inexpensive transition metal chalcogenides. The new MoS₂/CoSe₂ catalyst shows exceptional HER catalytic properties in acidic electrolyte with onset potential of mere -11 mV, a small Tafel slope of 36 mV per decade and a high exchange current density, representing the first non-noble metal catalyst that approaches the performance of state-of-the-art Pt/C catalyst. Inspired by the Nature using transition metals as catalytically active site to construct effective HER catalysts (for example, hydrogenase enzymes)^{5,36}, we believe that our study here will facilitate the development of newly efficient HER catalysts based on transitional metal chalcogenides.

Methods

Synthesis of CoSe₂/DETA nanobelts and MoS₂/CoSe₂ hybrid. All chemicals are of analytical grade and were used as received without further purification. First, ultrathin lamellar mesostructured CoSe₂/DETA nanobelts were prepared by our recently developed method²⁰. Briefly, 0.249 g Co(OAc)₂ · H₂O and 0.173 g Na₂SeO₃ were added into a mixed solution (40 ml) with a volume ratio of $V_{\text{DETA}}/V_{\text{DIW}} = 2:1$ (DIW, deionized water). The obtained wine solution was then transferred into a 50 ml Teflon-lined autoclave, which was sealed and maintained at 180 °C for 16 h. The resulting black floccules were collected by centrifugation (4,000 r.p.m. for 5 min) and washed by absolute ethanol for three times, and the resulting CoSe₂/DETA nanobelts were dried for next use. To prepare the MoS₂/CoSe₂ hybrid, 10 mg freshly made CoSe₂/DETA nanobelts and 10 mg (NH₄)₂MoS₄ were dispersed in 10 ml DMF and sonicated for 15 min under ambient conditions. Then, 0.05 ml N₂H₄ · H₂O was added into the suspension. After sonicating for another 15 min to dissolve completely, the mixed solution was transferred into a 50 ml Teflon-lined autoclave, which was sealed and heated in an oven at 200 °C for 10 h and then

cooled to room temperature naturally. The resulting black product was collected by centrifugation (7,000 r.p.m. for 8 min), then washed at least four times by distilled water and absolute ethanol to remove ions and possible remnants, and dried under vacuum at 80 °C for 6 h.

Synthesis of free 3D MoS₂ sheet aggregates. The synthetic procedure of free 3D MoS₂ sheet aggregates is the same with that for preparing MoS₂/CoSe₂ hybrid, the only difference is that no CoSe₂/DETA nanobelt substrates were added during the synthesis.

Characterization. The samples were characterized by different analytic techniques. X-ray powder diffraction (XRD) was carried out on a Rigaku D/max-rA X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å); TEM images, HRTEM images, SAED and an energy-disperse X-ray spectrum (EDS) were taken with a JEOL-2010 transmission electron microscope with an acceleration voltage of 200 kV. STEM and EDX elemental mapping were performed on JEOL ARM-200F. The X-ray photoelectron spectra (XPS) were recorded on an ESCALab MKII XPS using Mg K α radiation exciting source. The Fourier transform infrared spectra were measured on a Bruker Vector-22 FT-IR spectrometer at room temperature. Nitrogen sorption was determined by Brunauer, Emmett and Teller measurements with an ASAP-2020 surface area analyzer (see Supplementary Fig. 8 for results). The degradation of external MoS₂ around CoSe₂ was determined by the inductively coupled plasma-atomic emission spectrometry analysis using an Atomscan Advantage (Thermo Ash Jarrell Corporation, USA) spectrometer.

Electrocatalytic study. Electrochemical measurements were performed at room temperature using a rotating disk working electrode made of GC (PINE, 5 mm diameter, 0.196 cm²) connected to a Multipotentiostat (IM6ex, ZAHNER elektrik, Germany). The GC electrode was polished to a mirror finish (No. 40-6365-006, Gamma Micro Polish Alumina, Buehler; No.40-7212, Microcloth, Buehler) and thoroughly cleaned before use. Pt wire and SCE were used as counter and reference electrodes, respectively. The potentials reported in our work were vs the RHE through RHE calibration described below.

The preparation method of the working electrodes containing investigated catalysts can be found as follows. In short, 5 mg of catalyst powder was dispersed in 1 ml of 3:1 v/v DIW/isopropanol mixed solvent with 40 μ l of Nafion solution (5 wt%, Sigma-Aldrich), then the mixture was ultrasonicated for about 30 min to generate a homogeneous ink. Next, 10 μ l of the dispersion was transferred onto the GC disk, leading to the catalyst loading ~ 0.28 mg cm⁻². Finally, the as-prepared catalyst film was dried at room temperature. For comparison, bare GC electrode that has been polished and cleaned was also dried for electrochemical measurement.

Before the electrochemical measurement, the electrolyte (0.5 M H₂SO₄) was degassed by bubbling pure hydrogen for at least 30 min to ensure the H₂O/H₂ equilibrium at 0 V vs RHE at a rotation rate of 1,600 r.p.m. The polarization curves were obtained by sweeping the potential from -0.7 to -0.2 V vs SCE at room temperature and 1,600 r.p.m. (to remove the *in situ*-formed H₂ bubbles on the RDE), with a sweep rate of 2 mV s⁻¹. The electrochemical impedance spectroscopy measurement was performed in the same configuration at open circuit potential over a frequency range from 100 kHz to 5 mHz at the amplitude of the sinusoidal voltage of 5 mV and room temperature (see Supplementary Fig. 10 for results). MoS₂/CoSe₂ and pure MoS₂-coated CFPs (Toray, 1 cm², catalyst loading 1 mg) were used as working electrodes to collect chronoamperometry data at the applied potential of -0.7 V vs SCE. The polarization curves were replotted as overpotential (η) vs log current ($\log j$) to get Tafel plots for assessing the HER kinetics of investigated catalysts. By fitting the linear portion of the Tafel plots to the Tafel equation ($\eta = b \log(j) + a$), the Tafel slope (b) can be obtained. All data were reported without iR compensation.

RHE calibration. In all measurements, we used SCE as the reference electrode. It was calibrated with respect to RHE. The calibration was performed in the high-purity hydrogen-saturated electrolyte with a Pt foil as the working electrode. Cyclic voltammetry was run at a scan rate of 1 mV s⁻¹, and the average of the two potentials at which the current crossed 0 was taken to be the thermodynamic potential for the hydrogen electrode reaction. In 0.5 M H₂SO₄ solution, $E_{\text{RHE}} = E_{\text{SCE}} + 0.28$ V.

DFT calculations. The computational modelling of the adsorption, activation and reaction processes involved in HER on MoS₂/CoSe₂ was performed by periodic DFT with the Vienna *Ab-initio* Simulation Package (VASP). MoS₂/CoSe₂ model-building details (Supplementary Figs 13–15), HER mechanism and relevant references are provided in the Supplementary Methods.

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Author contributions

S.-H.Y. and M.-R.G. conceived the idea. M.-R.G., Y.-R.Z. and Y.-F.X. planned and performed the experiments, collected and analysed the data. J.-X.L. and J.L. performed the DFT calculations. J.J. and Q.G. assisted with the experiments and characterizations. M.-R.G. and S.-H.Y. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

Additional information

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